

SCIENCE FOR GLASS PRODUCTION

UDC 666.762

RARE-EARTH ALUMINATE BASED CERAMIC

A. O. Merkushkin¹

Translated from *Steklo i Keramika*, No. 10, pp. 3–5, October, 2012.

Fine powders of aluminates of rare-earth elements (REE) are obtained by wet combustion. The solid-phase synthesis of lanthanum-gadolinium aluminate is studied. It is shown that the desired phase can be obtained at temperatures to 750°C. The firing regimes that make it possible to obtain REE-aluminate ceramic with low open porosity and relative density to 99% of the theoretical value are determined.

Key words: matrix material, actinide, perovskite, aluminate, rare-earth elements.

One of the main problems of atomic energy is how to handle liquid high-level wastes (HLW) from radiochemical processing of spent fuel from nuclear power plants. The long-lived radionuclides ($T_{1/2} > 15$ yr) present in HLW can be divided into two groups. It is shown in [1] that the second group is much more dangerous than the first group and to optimize the time and mass of the buried wastes it is best to separate the actinide fraction of the HLW, which depending on the technological process will be comprised of lanthanides — fission products — wholly or partially. It is shown in [2] that perovskite with composition $M^I M^{II} O_3$ can be used to immobilize the actinide fraction. In this structure the cation M^I is coordinated with twelve oxygen atoms and the cation M^{II} with six. Ordinarily, the cation M^I is somewhat larger than M^{II} . In order for such contact between M^I , M^{II} and O to be possible their ionic radii must satisfy the relation [3]

$$t = \frac{R_I + R_O}{R_I + R_{II}} \frac{1}{\sqrt{2}}, \quad (1)$$

where the coefficient t lies in the range 0.8–0.9. The perovskite structure is stable in this case. In addition, the total charge of the cations must equal 6 in order to compensate the oxygen charge. Since HLW contain a large amount of lanthanides, they can comprise the foundation of the matrix, while trivalent iron ions Fe ($R_{II} = 0.67$ Å) or Al ions ($R_{II} = 0.57$ Å) can be used as M^{II} . For M^I radius from 0.094 to 0.104 Å the parameter t assumes values in the range 0.80–0.84 for Fe and 0.84–0.8 for Al.

The production and properties of ceramic based on REE ferrites are described in [4].

One of the common methods of synthesizing the matrix is briquetting by means of uniaxial pressing followed by sintering. The simplicity of the equipment and low cost set this method apart from other methods, for example, hot pressing or induction melting. The aim of the present work was to obtain ceramics based on lanthanum and gadolinium with the compositions $LaAlO_3$ and $La_{0.6}Gd_{0.4}AlO_3$ and to study their properties. The second composition was chosen because the average ionic radius of the cations in the M^I position (1.00 Å) is close to that of the elements in the actinide fraction of the HLW (0.999 Å) containing lanthanides (from La to Tb) and trivalent actinides (predominately Am and Cm).

Wet firing was chosen as the method for obtaining the initial powders for synthesis of the ceramic [5, 6]. In this method a mixture of solutions of metal nitrates with a reducing agent, for example, citric and amino-acetic (glycine) acids, β -alanine, hydrazine nitrate and so forth, is heated.

Chemically pure grade lanthanum and aluminum nitrates were used as the initial compounds. Gadolinium nitrate was obtained by dissolving gadolinium oxide in nitric acid. A weighed amount of glycine (Gly : $NO_3^- = 1.0 - 1.2$) was added to the mixed solution of metal nitrates. The solution was evaporated in a quartz vessel placed in a tubular furnace at temperature 280–300°C. An exothermal oxidation-reduction reaction completed the process. In this process the reaction mixture was heated and a large quantity of gaseous products released. After synthesis the powder was kept in a muffle furnace for 1 h at 700°C in order to remove the products of decomposition of glycine and to burn out carbon.

¹ D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia (e-mail: polaz@mail.ru).

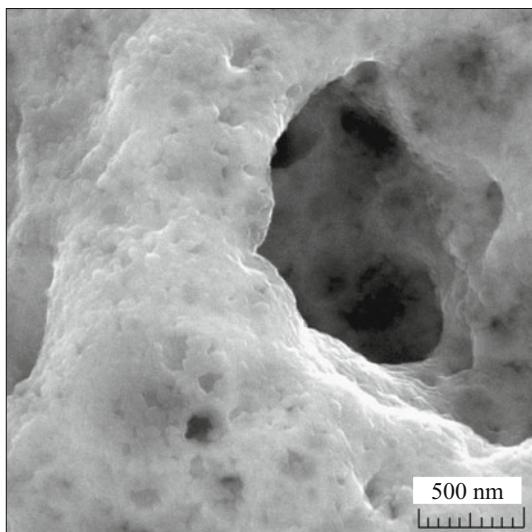


Fig. 1. SEM image of LaAlO_3 powder.

The powders obtained consisted of porous aggregates comprised of individual particles. The average particle size calculated from the specific surface area ($28 - 32 \text{ m}^2/\text{g}$) was about 30 nm. This value agrees with data obtained by scanning electron microscopy (Fig. 1).

X-ray phase analysis of the initial powders heated for 1 h at different temperatures showed that the LaAl_3 and $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ phases with a hexagonal unit cell form in the temperature range $700 - 800^\circ\text{C}$. As temperature is increased to 1200°C the phase composition of the powder remains unchanged (Fig. 2). In the case of $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ powder the reflections are shifted to large angles (compared with LaAlO_3), indicating that the cell parameters have decreased as a result of a decrease of the ionic radius from La (0.104 nm) to Gd (0.94 nm). The reflections of the individual oxides La_2O_3 , Al_2O_3 and Gd_2O_3 were not found in any diffraction patterns.

The powders obtained were subjected to disaggregation in a planetary mill by the wet method for 1 h (balls : material : water = 30 : 1 : 1). Laser-diffraction measurements showed the particle size to be $0.86 \mu\text{m}$; 90% of the particles did not exceed $0.86 \mu\text{m}$ in size.

A solution of polyvinyl alcohol (PVA) was introduced into the suspension. The mass fraction of PVC in terms of dry press-powder was 2 – 2.5%. The powders were dried at 100°C to residual moisture content 4 – 5%. The prepared powders were formed by uniaxial pressing into 1 – 2 mm thick and 12.0 mm in diameter cylindrical pellets under pressure 360 MPa or $4 \times 4 \times 60$ mm rectangular bars under pressure 360 MPa.

The past history of heat-treatment of the initial powder is well known to have a large effect on the behavior of pressed samples during kilning. In order to find the optimal preliminary heating temperature a series of experiments was conducted using powder with stoichiometric composition

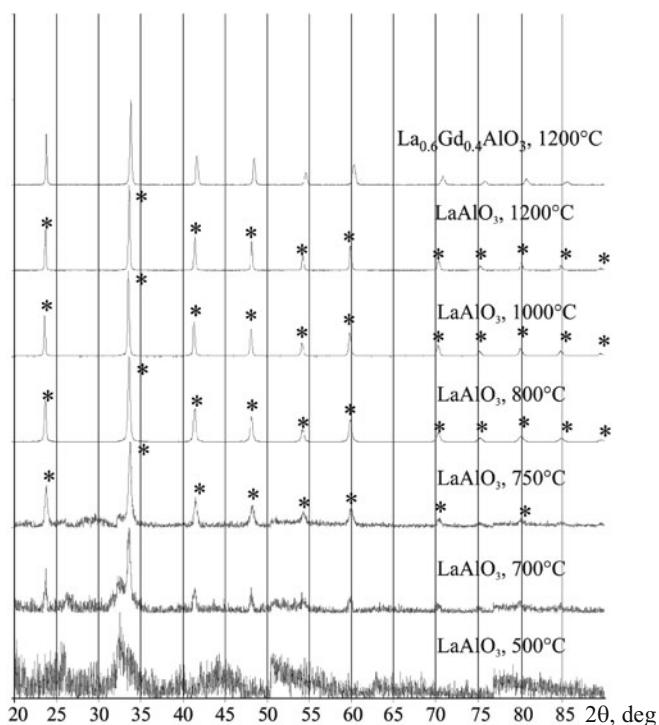


Fig. 2. X-ray diffraction patterns of LaAlO_3 and $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ powders heated at different temperatures. An asterisk (*) indicates the LaAlO_3 phase with hexagonal symmetry.

$\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$. The powders obtained by “wet combustion” were soaked for 1 h at 750°C and then additionally at different temperatures (900 to 1100°C) for 1 h. The heat-treated powders were disaggregated in a planetary mill, a temporary process binder was introduced and parts were pressed as described above.

The behavior of the samples during kilning was studied by dilatometry, i.e., recording shrinkage curves during the time the samples are heated uniformly to a prescribed temperature. The temperature at which the shrinkage rate assumed its maximum value $t_{\max dL/dT}$ and the shrinkage onset temperature $t_{\text{on.shrin}}$ are presented in Table 1.

The shrinkage onset temperature assumes its minimum value (1180°C) for blanks pressed from powder heat-treated at 1000°C . This is 40°C lower than for powders heat-treated at other temperatures. The temperature corresponding to the highest shrinkage rate is lowest (1430°C) for the sample fabricated from powder heat-treated at 900°C , i.e., the maxi-

TABLE 1. Shrinkage of the samples during kilning

| Heat-treatment temperature, $^\circ\text{C}$ | $t_{\max dL/dT}$, $^\circ\text{C}$ | $t_{\text{on.shrin}}$, $^\circ\text{C}$ |
|--|-------------------------------------|--|
| 750 | 1510 | 1220 |
| 900 | 1450 | 1220 |
| 1000 | 1460 | 1180 |
| 1000 | 1460 | 1180 |

TABLE 2. Results from studying the Kilning Regimes

| Composition | <i>t</i> , °C | ΔD , % | <i>W</i> , % | P_{op} , % | ρ , g/cm ³ (%*) |
|--|---------------|----------------|--------------|--------------|---------------------------------|
| $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ | 1350 | 13.8 | 2.63 | 13.7 | 5.561 (83) |
| | 1375 | 15.7 | 2.07 | 10.8 | 5.732 (88) |
| | 1400 | 18.6 | 0.78 | 4.9 | 6.217 (90) |
| | 1450 | 19.1 | 0.06 | 0.4 | 6.627 (96) |
| | 1500 | 19.0 | 0.08 | 0.5 | 6.716 (98) |
| | 1550 | 19.4 | 0.06 | 0.4 | 6.759 (98) |
| LaAlO_3 | 1350 | 13.8 | 2.98 | 15.5 | 5.427 (81) |
| | 1375 | 15.7 | 2.07 | 10.8 | 5.667 (87) |
| | 1400 | 17.3 | 0.16 | 1.0 | 6.383 (98) |
| | 1450 | 19.1 | 0.09 | 0.6 | 6.402 (98) |
| | 1500 | 17.6 | 0.02 | 0.1 | 6.479 (99) |
| | 1550 | 18.7 | 0.00 | 0.0 | 6.508 (99) |

* Relative density as a percentage of the theoretical value.

mum rate of densification of this sample is reached at a lower temperature. For this reason, the heat-treatment temperature 900°C was chosen as optimal, and it was used in subsequent experiments on optimizing the kilning regime.

The variable parameter for studying the sinterability of lanthanum aluminate LaAlO_3 and lanthanum-gadolinium aluminate $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ ceramics was the kilning temperature. The kilning time (3 h) and the temperature rise rate (5 K/min) remained constant. The comparison parameters were the radial shrinkage ΔD , water absorption *W*, open porosity P_{op} and density ρ . The results of the study of kilning regimes are presented in Table 2. The theoretical density was chosen on the basis of the unit cell parameters calculated from the diffraction data. The values for LaAlO_3 and $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ were 6.525 and 6.890 g/cm³, respectively.

The $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$ ceramic reaches relative density 98% of the theoretical value and open porosity no greater than 0.5% at 1500°C. The grain size obtained for the ceramic under these conditions is 2–5 μm (Fig. 3). The crystals fit tightly together, forming individual clusters.

Pure lanthanum aluminate ceramic (no gadolinium) reaches relative density 99% of the theoretical value and open porosity no greater than 0.6% at 1450°C.

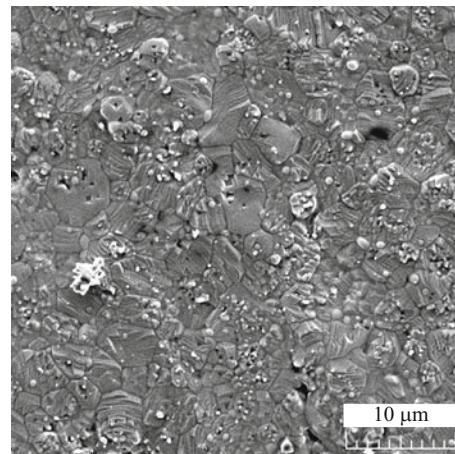


Fig. 3. SEM image of the surface of the ceramic $\text{La}_{0.6}\text{Gd}_{0.4}\text{AlO}_3$.

In summary, the optimal kilning regime for the ceramic based on REE aluminates is 1450–1500°C, 3 h. The ceramic obtained under these conditions possesses low open porosity (to 0.6%) and relative density 98–99% of the theoretical value.

REFERENCES

1. N. S. Babaev, A. O. Merkushkin, A. V. Ochkin, and S. I. Rovnyi, “Calculation of the setting time of the radiation equivalence of high-level wastes,” *At. Énerg.*, **98**(2), 123–129 (2005).
2. O. A. Merkushkin, A. V. Ochkin, S. I. Rovnyi, and S. V. Stepanovskii, “ $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{O}_3$ perovskite as a matrix for inclusion of the actinide fraction of HLW,” *Radiokhim.*, **51**(2), 170–174 (2009).
3. F. S. Galasso, *Structure, Properties and Preparation of Perovskite-Type Compounds*, Pergamon Press, Oxford (1969).
4. A. O. Merkushkin and Zo E Mo, “Ceramic based on REE ferrites,” *Steklo Keram.*, No. 11, 25–27 (2011); A. O. Merkushkin and Zo E Mo, “UREE-ferrite based ceramic,” *Glass Ceram.*, **68**(9–10), 337–339 (2011).
5. K. Deshpanda, A. Mukasyan, and A. Varma, “Direct synthesis of iron oxide nanopowders by the combustion approach: reaction mechanism and properties,” *Chem. Mater.*, **16**, 4896–4904 (2004).
6. K. Deshpanda, A. Mukasyan, and A. Varma, “Aqueous combustion synthesis of strontium-doped lanthanum chromite ceramics,” *J. Am. Ceram. Soc.*, **86**(7), 1149–1154 (2003).